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(54) Dental composite and porcelain repair.

(57) A filled-resin composition useful for porcelain repair and as a dental composite and therefore made up of non-toxic materials and a method for repairing porcelain or teeth. The composition comprises a methacrylate functional resin usable in dental composites, powdered filler-colorant therein, at least one photoinitiator for the resin in an amount sufficient to initiate polymerization and complete it in depth within about half a minute when exposed to a visible-light output of at least 5,000 foot candles, the photoinitiator being an exciplex of (1) either 1,3-boronedione or benzil and (2) either ethyl-4-dimethyl amino benzoate or ethyl-2-dimethyl amino benzoate, and at least one accelerator-free peroxide curing agent for the resin in an effective amount for completing polymerization within about one-half hour of any portion of the resin not receiving sufficient light to effectuate complete cure before then. The method comprises mixing the components together under ordinary indoor lighting conditions, emplacing the mixture within a few minutes of the mixing, and curing at least a substantial portion of the emplaced mixture *in situ* for one half-minute under intense visual-light illumination of at least 5000 foot-candles. Any resin then uncured by light is cured within the next half hour by the peroxide curing agent.

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## DENTAL COMPOSITE AND PORCELAIN REPAIR

S P E C I F I C A T I O N

This invention relates to dental composites and porcelain repair material and to methods for making them.

Background of the Invention

Over the years many dental composites have been introduced, each composite possessing certain physical properties. However, substantially all of these dental composites can be categorized into two main groups, self-cured materials and light-cured materials.

The self-cured composites have involved free radical polymerization initiated by benzoyl peroxide (or another suitable peroxide) and accelerated, typically by a tertiary amine such as N,N-dimethyl-p-toluidine. The curing agents must be stored separately from the resin they are to cure, and they are mixed together just before use.

The light-cured composites have involved free radical polymerization initiated by the photoexcitation of light-sensitive compounds by ultraviolet or visible light. They are single-component systems, typically pastes, stored in opaque containers until the time of cure. Some of the photoinitiators that have been employed are the benzoin ethers, benzil ketals, dialkoxyacetophenones, benzophenones, thioxanthenes, and hydroxyalkylphenones.

In the practice of dentistry, some tooth repairs have been better achieved by self-cured composites and some have been better achieved by light-cured composites. While many factors have helped to determine whether a dentist would or should choose a self-cured material or a light-cured material, the prime factors have been working time, setting time, and the architecture of the cavity preparation.

1           The light-cured composites, combined with special  
2 high-lumen lighting units employing fiber optics, have  
3 offered variable working times and fast "snap" sets.  
4 Setting can take between ten and forty seconds in many  
5 instances. However, the use of light-cured composites has  
6 been limited by the depth of the repair and the ease of  
7 light penetration. Relatively unobstructed, clean, shallow  
8 repair surfaces have been required. Visible-light-cured  
9 materials have helped in solving some of the limitations  
10 caused by repair depth, by roughly doubling the depths at  
11 which cure is effective as compared to ultra-violet light-  
12 cured material. Also, many dentists have felt more  
13 comfortable using a visible, as opposed to an ultra-  
14 violet, activating light source.

15           The amount of cure is variable and is a function  
16 of exposure to lumens of visible light. These facts result  
17 in extremely dangerous situations in many dental  
18 restorations; because most dentists do not realize this  
19 deficiency, because light-cured systems are advertised to  
20 be able to be cured through tooth structure. In reality,  
21 the situation is, at best, a gradient level of cure  
22 obtained in relation to the amount of lumens of light  
23 energy available to the restorative resin. That is to say,  
24 layers close to the light source undergo greater percent  
25 polymerization than the underlying layers. Consequently,  
26 the incompletely polymerized restoration may wash out,  
27 leak, or fail in adhesion. Yet the surface or bulk of the  
28 restoration may appear clinically adequate, even though  
29 new secondary decay may be beginning, and, because of its  
30 concealment, result in death of the pulp or loss of the  
31 tooth.

32           When a light-cured resin liner is used with a  
33 light-cured paste composite at a depth of around 3 mm. or  
34 greater, the resin liner may not cure because of  
35 insufficient light reaching the resin. Uncured resin  
36 liner can cause leaching, pulpal irritation, and loss of

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1 adhesion. Heretofore, the resin liner had, therefore, to  
2 be polymerized prior to placement of the composite. With  
3 this invention, such double cure is unnecessary.

4         Self-cured systems have offered assurance of  
5 polymerization throughout the polymer mass used in any  
6 repair surface architecture. However, their use has been  
7 limited by manufacturer-determined work times and set  
8 times. The peroxide and the accelerator could be adjusted  
9 to give widely varying setting times; the quicker the set  
10 time, the quicker the placement had to be made. Thus, in  
11 order to give enough time for accurate placement, the set  
12 times had to be longer than were desirable. Generally, set  
13 times have been at least two or three minutes after mix,  
14 and placement has had to be completed within forty-five  
15 seconds after mix. This had made dentists work somewhat  
16 faster than was desirable for many placements, and even  
17 then the patient had to be immobilized longer than was  
18 desirable before the composition set.

19         This invention overcomes the deficiencies of  
20 light-cured systems, while preserving their functional  
21 benefits. It also overcomes the deficiencies of the self-  
22 cured systems by enabling quicker set times coupled with  
23 longer placement times, if desired.

24         The system of this invention thus offers the best  
25 properties of both types of curing systems without suffer-  
26 ing from the limitations of either, and therefore it  
27 significantly advances the practice of dentistry and the  
28 science of dental materials.

29         The system of the present invention can be in a  
30 powder-liquid, paste-paste, paste-powder, or gel-powder  
31 form, so that there is no loss in versatility of possible  
32 embodiments.

33         Similar problems occur with porcelain repair  
34 systems in general, not only in dental uses, but for  
35 repairing such porcelain articles as bathtubs, and the  
36 invention solves these problems also.

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1 Summary of the Invention

2       This invention comprises a composite system  
3 combining a small amount of peroxide curing agent, free  
4 from accelerator, with certain photoinitiator systems  
5 called exciplexes. A two-component system is required,  
6 with mixture just before use. Conveniently, the resin and  
7 its exciplex members can be stored in opaque (preferably  
8 black) containers as one component, with or without some  
9 of the filler. The peroxide is stored in a separate  
10 component, including much or all of the filler-colorant,  
11 in a container which need not be opaque. The two  
12 components are mixed just prior to application, and there  
13 is a wide latitude of mixing time, because no accelerator  
14 is used. The curing effect of the peroxide in the resin is  
15 quite slow, while the exposure of the resin and photo-  
16 initiator exciplex members in ordinary light--whether  
17 daylight or artificial light--will not result in  
18 substantial curing. The time for placement is not  
19 critical, because neither the photoinitiator exciplex nor  
20 the peroxide causes quick curing at this stage. After  
21 placement, a high-lumen light source is used with a fiber-  
22 optics bundle to effect rapid cure (typically, ten to  
23 forty seconds) down to a substantial depth. If the cavity  
24 being filled is deeper than that depth, or if some of the  
25 placed material has been shaded from the light or not  
26 adequately illuminated, the light alone does not effect  
27 sufficient cure. However, the cured deposit covering the  
28 uncured material holds the uncured material in place, and  
29 the peroxide has been found to effect cure of the uncured  
30 material in about an hour, and usually in about half that  
31 long.

32       To explain exciplexes: as in photoinitiator  
33 systems generally, absorption of light by the ketone group  
34 of some photoinitiators results in promotion of the  
35 photoinitiator to a chemically reactive excited state;  
36 alpha-cleavage results, and free radicals are formed. "In  
37 the case of appropriate donor/acceptor systems,  
38

1 interaction between an electronically excited molecule and  
2 a ground-state molecule of another type may form an  
3 excited-state complex, termed an 'exciplex'." Roffey, C.  
4 G., Photopolymerization of Surface Coatings, p. 70, John  
5 Wiley and Sons, Ltd., New York, 1982.

6 The incorporation of a suitable peroxide,  
7 preferably benzoyl peroxide, with the photoinitiated  
8 composite system has a synergistic effect on the free-  
9 radical polymerization, resulting in uniform cure without  
10 limitation after exposure to the activating light source.  
11 The peroxide content is preferably about 0.05% to about  
12 0.3% of the total composition.

13 The exciplex photoinitiators of this invention are  
14 a combination of (1) either 2,3-bornanedione or benzil and  
15 (2) either ethyl-4-dimethyl amino benzoate or ethyl-2-  
16 dimethyl amino benzoate. The amount should be enough to  
17 initiate polymerization in the selected resin and complete  
18 it in depth within about half a minute when the filled-  
19 resin composition is exposed to a visible-light output of  
20 at least 5,000 foot candles. The peroxide should be  
21 present in amount sufficient to complete, within about an  
22 hour, the resin's polymerization, where it is not  
23 completed by the photoinitiator-derived action, as where  
24 the light never reaches the resin in the needed amount.

25 Thus, suitable photoinitiators for this invention  
26 are the following exciplex-forming photoinitiators:

27  
28 2,3-Bornanedione with ethyl-4-dimethyl amino  
29 benzoate

30  
31 2,3-Bornanedione with ethyl-2-dimethyl amino  
32 benzoate

33  
34 Benzil with ethyl-4-dimethyl amino benzoate

35  
36 Benzil with ethyl-2-dimethyl amino benzoate.

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1           There are, of course, many other compounds capable  
2 of photoinitiation. Many of these are taught in U.S.  
3 4,222,835, to Dixon. However, Dixon's formulations were  
4 intended for industrial fabrication, whereas the present  
5 invention involves formulations which can be left in the  
6 human mouth for many years. Consequently, compounds which  
7 are known or are suspected to be toxic, carcinogenic,  
8 teratogenic, mutagenic, etc. are not considered.

9           In addition there are those disclosed in our  
10 earlier filed and co-pending application Serial Number  
11 83 104316.1, filed 2 May 1983.

12           The present invention provides a much deeper cure  
13 than do light-cured composites and obtains a much more  
14 uniform degree of cure than do such systems. It obtains a  
15 certainty of cure under overhangs, as opposed to prior-art  
16 light-cured composites, and a more reliable cure through  
17 tooth structure than the prior-art light-cured composites.  
18 It provides more uniformity of cure, regardless of  
19 exposure time or intensity. It provides better adhesion to  
20 the teeth or to substrates such as porcelain as used in  
21 dentistry and in plumbing fixtures, apparently due to more  
22 complete polymerization. It has a longer shelf-life than  
23 self-cured composites. It has better physical properties  
24 than most prior-art light-cured composites, especially  
25 lower water absorption.

26           It does not develop color bodies in composites  
27 using chemically active glasses, such as strontium glass,  
28 where some curing systems do develop objectionable color.  
29 Moreover, the composite, when installed and cured in a  
30 dental environment, looks like the tooth, not only in  
31 ordinary light but also in ultra-violet light. In ultra-  
32 violet light it fluoresces to substantially the same  
33 degree as the tooth itself.

34           As stated above, the product is made up of two  
35 separate formulations, one containing all or much of the  
36 material to be cured along with the exciplex photoinitia-  
37 tors. This formulation is kept from light, as in an  
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1 opaque container. The other formulation contains the  
2 peroxide curing agent, preferably along with any  
3 ingredient not itself cured thereby, such as the filler-  
4 colorants. In many instances (as in paste-paste systems)  
5 it is preferred that the composition be so formulated that  
6 equal amounts of the two formulations are mixed together  
7 when they are to be used. In powder-liquid systems, there  
8 is usually two to three and one-half as much powder as  
9 liquid in each mixture.

10

11 Description of Some Preferred Embodiments

12

13 The binders or resins to be cured comprise  
14 substantially all of those currently used in dental  
15 composites. These are all methacrylate-functional resins.  
16 Typical is ethoxylated bisphenol-A-dimethacrylate. Others  
17 include Bis-GMA and the adducts disclosed in Waller's U.S.  
18 Patent No. 3,629,187. Mixtures of resins may be used.  
19 Waller's adducts are of 2-2'-propane bis [3-(4-phenoxy)-  
20 1,2-hydroxy propane-1-methacrylate] and a mono- or di-  
isocyanate.

21

22 The curing agents, as said, are of two types:  
23 peroxides and photoinitiators. A suitable and preferred  
24 peroxide is benzoyl peroxide. Some other peroxides are  
25 either inoperable or have dangerous toxic side effects.

26

27 The photoinitiators are ordinarily in the same  
28 component as the resin or gel, the resin-(or gel)-photo-  
29 initiator exciplex components mixture being kept in opaque  
30 containers until use. The peroxide is ordinarily kept  
31 separate from the resin, usually with or upon the filler-  
32 colorant or most of the filler-colorant. In paste-paste  
systems, some of the resin may be in the same component as  
the peroxide.

33

34 The suitable exciplex-forming photoinitiators are  
the following:

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2,3-Bornanedione with ethyl-4-dimethyl amino  
benzoate

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1           2,3-Bornanedione with ethyl-2-dimethyl amino  
2           benzoate

3  
4           Benzil with ethyl-4-dimethyl amino benzoate

5  
6           Benzil with ethyl-2-dimethyl amino benzoate.

7  
8           To the best of our knowledge, no one has  
9 previously suggested that the combination of any of these  
10 light-curing exciplex photoinitiators with any peroxide  
11 could bring about better curing of these dental resins.  
12 Likewise, it is not ordinary to utilize peroxide in such  
13 small amounts as those utilized in this invention to  
14 initiate polymerization of these resins. Furthermore,  
15 peroxide curing agents are conventionally employed with  
16 accelerators, and no accelerator is used here.  
17 Consequently, the results obtained by this invention were  
18 totally unexpected.

19           Practically all inert filler-colorants currently  
20 used or usable in dental composites are usable herein.  
21 Preferably, they are neither too coarse nor too fine. The  
22 compositions employed in this invention may contain at  
23 least about 10% by weight and up to about 90% by weight,  
24 and preferably about 70-80% by weight, of a finely  
25 divided, inert inorganic filler-colorant. The filler-  
26 colorant, which may be in the form of spheres, platelets,  
27 fibers, whiskers, or particles of any regular or irregular  
28 shape and which preferably is transparent or translucent,  
29 may comprise for example, apatite, soda glass, barium  
30 glass, strontium glass, borosilicate glass, silica, fumed  
31 silica, flint silica, alumina, quartz, lithium aluminum  
32 silicate, or the like. Mixtures of more than one filler-  
33 colorant may be used. The particle size of the filler-  
34 colorant may range from about 0.005 to about 0.5 microns  
35 in the case of microfine silica, to not greater than about  
36 500 microns in the case of irregularly shaped particles.  
37 Further, a range of particles sizes may be used. Where the

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1 filler-colorant is in the form of fibers, the maximum  
2 dimension of the fibers preferably is not greater than  
3 about 110 microns. On the other hand, where the filler-  
4 colorant is in the form of spheres or platelets or is  
5 irregularly shaped, the maximum dimension of the particles  
6 preferably is not greater than about 350 microns.

7       The identity of the filler-colorant is not  
8 critical, but barium-containing glass (hereinafter called  
9 "barium glass"), strontium-containing glass (hereinafter  
10 called "strontium glass"), lithium aluminum silicate,  
11 flint silica, and fumed silica are excellent fillers and  
12 mixtures of these are usually preferable to the use of  
13 just one of them. For example, lithium aluminum silicate  
14 has a negative heat coefficient of expansion, giving lower  
15 overall thermal dimensional changes to the composite.  
16 Barium and strontium glass impart opacity to X-rays. Flint  
17 silica imparts tooth-like color, and fumed silica adjusts  
18 viscosity and improves polishability.

19       One example of barium glass is Ray-Sorb T-2000, a  
20 product of Kimble Division of Owens-Illinois Glass  
21 Company. The same company makes Ray-Sorb T-4000, an  
22 example of strontium glass.

23       Preferably, the peroxide is dispersed on the  
24 filler-colorant powder, or by being dissolved in a  
25 suitable solvent, is sprayed on the filler-colorant  
26 powder, and the solvent evaporated. Preferably, the  
27 peroxide is deposited in combination with a silane, such  
28 as gamma-methacryloxy propyl trimethoxy silane (sold by  
29 Union Carbide as A-174 silane), which is used to improve  
30 bonding between the filler and the resin. The benzoyl  
31 peroxide and the silane may be dissolved in methylene  
32 chloride, chloroform, ether, or acetone, for example. Then  
33 a slurry is made with the powdered filler-colorant; the  
34 solvent is stripped off, leaving the silane and the  
35 peroxide deposited on the dry powder filler-colorant.

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1           Glacial acetic acid is often used, in very small  
2 amounts, because the hydrolysis reaction which attaches  
3 the silane molecule to the filler-colorant particle is  
4 carried out most effectively at a pH slightly less than  
5 neutral.

6           Butylated hydroxytoluene is sometimes used in  
7 order to scavenge small amounts of free radicals which can  
8 form during extended shelf storage.

9           The invention can assume several forms: a powder-  
10 liquid form, a paste-paste form, a paste-powder form, and  
11 a gel-powder form. These forms will be considered in  
12 order.

#### 13 14 Powder-liquid systems

15           In general, the powder in this form comprises a  
16 suitable filler-colorant material, a suitable silane, such  
17 as gamma-methacryloxy propyl trimethoxy silane, and a  
18 suitable peroxide curing agent such as benzoyl peroxide.  
19 Preferably, these ingredients are in the following  
20 approximate range of proportions by weight:

21		
22	<u>Powder</u>	
23		
24	<u>Ingredients</u>	<u>Percentage by Weight</u>
25	Filler-colorant	99.85 to 97.70%
26	Silane	0.10 to 1.55%
27	Peroxide curing agent	0.05 to 0.70%
28	Glacial acetic acid	0.00 to 0.05%

29  
30 As stated above, the filler-colorant may be a mixture of  
31 some or several of the filler-colorants listed above, or  
32 it may be just one type of filler.

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1        Liquid

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<u>Ingredients</u>	<u>Percentage by Weight</u>
Resin	99.93 to 81.95%
Photoinitiator exciplex	0.7 to 18%
Butylated hydroxy toluene	0.00 to 0.05%

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8            The formulae may be further generalized in a  
9 somewhat more specific manner as follows: it being  
10 understood that the various types of ingredients (e.g.,  
11 filler-colorant, resin, etc.) will be used in quantities  
12 that will total to the amounts just spelled out above:

13

14        Powder:

15

<u>Ingredients</u>	<u>Percentage by Weight</u>
Barium glass	0 to 30
Lithium aluminum silicate	0 to 99.85
Flint silica	0 to 10
Borosilicate glass	0 to 99.85
Custer feldspar	0 to 10.00
Fumed synthetic silica	0 to 99.85
Quartz	0 to 99.85
Titanium dioxide	0 to 0.15
Tinting agents	
(e.g., iron oxides)	0 to 5
A-174 Silane	0.1 to 1.55
Peroxide curing agent	0.05 to 0.70
Glacial acetic acid	0 to 0.05

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1        Liquid

3	<u>Ingredients</u>	<u>Percentage by Weight</u>
4	Bis-GMA	0        to 80
5	Ethoxylated bisphenol-A-	
6	dimethacrylate	0        to 99.3
7	Ethylene glycol	
8	dimethacrylate	0        to 60
9	Diethylene glycol	
10	dimethacrylate	0        to 60
11	Triethylene glycol	
12	dimethacrylate	0        to 60
13	Polyethylene glycol	
14	dimethacrylate	0        to 60
15	Photoinitiator (one or	
16	more from the exciplex	
17	list above)	0.7    to 18
18	Butylated hydroxy toluene	0        to 0.05

19

20            Tinting agents are used to impart a more tooth-

21 like color. Red and yellow iron oxides are usually

22 employed.

23            Storage life for each mixture is very long, no

24 deterioration having been noticed so far over a period of

25 two and one-half years. The powder and the liquid are

26 mixed together in a ratio of weight from about 1:1 to

27 about 4:1 powder to liquid, just before they are needed.

28 Mixing may be accomplished on a paper mixing pad, with a

29 plastic instrument. Mixing may be done under normal room

30 lighting conditions, as found in the dental operatory,

31 illumination typically varying in intensity from about 80

32 to about 100 foot candles. Under these conditions, the

33 paste begins to gel after about 10 to 30 minutes,

34 depending on the particular formulations and

35 illuminations.

36

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1           When it is desired to initiate curing, the mixed  
2 material is exposed to the output from a dental visible  
3 light curing unit. For all examples cited herein, a Visar  
4 curing light, marketed by Den-Mat, Inc., Santa Maria,  
5 California, was used. This unit utilizes a type EKE or EJW  
6 quartz-halogen light bulb, operating at 21 VAC. The light  
7 is transmitted to the work site by a flexible fiber-optic  
8 bundle, 1/4 inch in diameter by four feet in length. Other  
9 units are available from other manufacturers. All are  
10 similar in principle and results. Results of these  
11 examples would be expected to differ only in degree if  
12 other units were used. The output of the Visar unit used  
13 is  $180 \times 10^4$  Candella per square meter, giving illumina-  
14 tion of about 20,000 foot candles on the material being  
15 cured. Satisfactory operability can be achieved with 5,000  
16 foot candles.

17           Under these conditions, the material cures in from  
18 10 seconds to 30 seconds, with a cured depth of from 0.60  
19 to 5.60 mm. Upon further standing, that is, from 5 minutes  
20 to 35 minutes, the material exhibits a cure depth of  
21 greater than 12 mm. It shows a tensile strength, measured  
22 by the diametral method on samples 6 mm diameter by 3 mm  
23 high, of between 4800 psi and 7000 psi. A popular prior-  
24 art, light-cured dental composite, when tested in  
25 identical fashion, showed a cure depth of 3.05 mm  
26 immediately after exposure to the curing light, but this  
27 cure depth did not increase over a period of 16 hours  
28 after cure, and its diametral tensile strength was only  
29 2030 psi.

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1 EXAMPLE 1

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3 Powder-Liquid System

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5 Powder:

6 <u>Ingredients</u>	Percentage by Weight
7 Barium glass	28.63%
8 Lithium aluminum silicate	67.84%
9 Flint silica	2.84%
10 Benzoyl peroxide	0.20%
11 A-174 silane	0.47%
12 Glacial acetic acid	0.02%

13  
14 A-174 silane is a Union Carbide product,  
15 chemically gamma-methacryloxy propyl trimethoxy silane.  
16 The barium glass may be Ray-Sorb T-2000, a product of  
17 Kimble Division of Owens-Illinois Glass Company or may be  
18 barium aluminum silicate.

19  
20 Liquid

21 <u>Ingredients</u>	Percentage by Weight
22 Ethoxylated bisphenol-A-	
23 dimethacrylate	95.53%
24 2,3-Bornanedione	0.17%
25 Ethyl-4-dimethylamino-	
26 benzoate	4.30%

27  
28 The powder and the liquid were mixed together,  
29 preferably in a ratio by weight of about 2:1 to about  
30 3-1/2:1, powder to liquid, just before they were needed.  
31 Mixing took about twenty seconds. The mixtures are  
32 preferably applied within about five minutes. The setting  
33 time was about twenty minutes when not exposed to a dental  
34 curing light, but was less than thirty seconds on exposure  
35 to a dental curing light. The result was a hard filling.

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1 EXAMPLE 2

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3 Hardness comparisons with some prior-art systems:

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5 A disk of a commercially available light-curable  
6 dental composite was prepared, 20 mm diameter by 1 mm  
7 thick. One-half of this disk was shaded with aluminum  
8 foil, and the disk then was placed under a photoflood lamp  
9 for 15 minutes. The sample was removed from under the  
10 lamp, the foil removed from the sample, and Barcol  
11 hardness measured on both the shaded and unshaded halves.  
12 The unshaded half showed a Barcol hardness of 82, while  
13 the shaded side had a Barcol hardness reading of less than  
14 1. This same experiment was performed on a disk made of  
15 the mixed but uncured material of Example 1, and both  
16 sides of both disks showed a Barcol hardness of 92.  
17

18 EXAMPLE 3

19  
20 Comparison of degree of cure:

21  
22 A series of tests was performed on several  
23 commercially-available light-curing composites to  
24 determine the degree of cure of the resin matrix. Testing  
25 was accomplished by preparing duplicate samples, 1 mm  
26 thick by 40 mm in diameter. These samples were cured by  
27 exposing them to a photoflood lamp for 30 minutes, and  
28 then they were placed in 37°C. water for 24 hours. The  
29 samples were then dried, and placed in a desiccator and  
30 weighted daily until constant weight ( $\pm 0.5$  mg.) was  
31 achieved. The samples were then granulated, placed in a  
32 glass thimble and extracted for 12 hours in a Soxhlett  
33 extraction apparatus with methylene chloride. After  
34 extraction, the samples were weighted and the weight loss  
35 converted to percent uncured monomer removed.  
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1           When two popular commercially-available light-  
2 cured dental composites were tested in this manner, the  
3 cured product contained 3.08% and 5.26% extractables,  
4 representative of the amount of uncured monomer.

5           The material of Example 1 of this invention, when  
6 tested in the same manner, contained only 1.87%  
7 extractables, showing a much higher degree of cure.

8  
9   EXAMPLE 4

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11   Comparison of degree of water sorption:

12  
13           A series of three light-cured dental restoratives  
14 were tested in order to determine the degree of water  
15 sorption. Samples were in duplicate, and were configured  
16 and tested in accordance with American Dental Association  
17 Specification No. 27.

18           Two popular commercially-available light-cured  
19 dental restoratives were found to have water sorption  
20 values of 1.05 and 0.95 mg/cm<sup>2</sup>, respectively. The material  
21 of Example 1 gave a value of only 0.86 mg/cm<sup>2</sup>.

22  
23   EXAMPLE 5

24  
25   Powder-liquid system of porcelain repair:

26  
27           The powder-liquid system of Example 1 was tested  
28 as a porcelain repair material, as described in U.S.  
29 Patent No. 4,117,595.

30           A commercially available material marketed to  
31 practice the above-mentioned patent had test results of  
32 2015 psi bond strength (average of 5 samples) when tested  
33 7 days after preparation, being stored meantime in water  
34 at 37°C.

35           The material of Example 1, when tested in the same  
36 fashion, with the same test equipment, gave results of  
37 2400 psi bond strength or 26.6% higher.

38

1 EXAMPLE 6

2

3       Comparison with a conventional powder-liquid system  
4 (using larger amounts of benzoyl peroxide than this  
5 system):

6

7       Powder:

8

9 <u>Ingredients</u>	<u>Percentage by Weight</u>
10       Strontium glass	
11       (Ray-sorb T-4000)	95.69%
12       A-174 Silane	1.44%
13       Benzoyl peroxide	2.87%

13

14       Liquid:

15

16 <u>Ingredients</u>	<u>Percentage by Weight</u>
17       Ethoxylated bisphenol-A-	
18       dimethacrylate	77.21%
19       Triethylene glycol	
20       dimethacrylate	19.31%
21       1-Hydroxy-4-methoxy-	
22       benzophenone	1.93%
23       Butylated hydroxytoluene	0.05%
24       N,N-2-hydroxyethyl-p-	
25       toluidine	1.50%.

25

26       The powder and liquid were mixed in a weight ratio  
27 of 3:1 of powder to liquid and cured properly. However, a  
28 bright green color was formed on curing. The mixture was  
29 repeated after acid-washing the strontium glass, but the  
30 green color persisted. The mixture was again repeated  
31 using N,N-3,5-tetramethylaniline as a substitute for the  
32 N,N-2-hydroxyethyl-p-toluidine. Again the green color  
33 developed.

34

35

36

37

38

1 The mixture was repeated once again using  
2 N,N-dimethyl-p-toluidine as activator instead of the  
3 N,N-2-hydroxyethyl-p-toluidine. This time the green color  
4 did not develop, but the curing characteristics of the  
5 composite degraded.

6 Then the experiment was repeated, using the  
7 following powder and liquid:

8  
9 Powder:

<u>Ingredients</u>	<u>Percentage by Weight</u>
Strontium glass	
(Ray-sorb T-4000)	98.300%
A-174 Silane	1.475%
Benzoyl peroxide	0.200%
Acetic acid	0.025%

16  
17 Liquid:

<u>Ingredients</u>	<u>Percentage by Weight</u>
Ethoxylated bisphenol-A-	
dimethacrylate	76.41%
Triethylene glycol	
dimethacrylate	19.10%
2,3-Bornanediol	0.17%
Ethyl 4-dimethyl amino	
benzoate	4.30%
Butylated hydroxytoluene	0.02%

28  
29 No color developed, the material cured satisfactorily  
30 under the output from a Visar dental curing light, and  
31 exhibited a depth of cure of 5.20 mm immediately after  
32 exposure to the light, and 12 mm depth of cure after 30  
33 minutes. Diametral tensile strength was 6000 psi.

1 EXAMPLE 7

2

3 Powder-Liquid System

4

5 Powder:

6	<u>Ingredients</u>	<u>Percentage by Weight</u>
7	Barium glass	28.63%
8	Lithium aluminum silicate	66.80%
9	Flint silica	2.84%
10	Benzoyl peroxide	0.20%
11	A-174 silane	1.51%
12	Glacial acetic acid	0.02%

13

14

15 Liquid

16	<u>Ingredients</u>	<u>Percentage by Weight</u>
17	Ethoxylated bisphenol-A-	
18	dimethacrylate	95.53%
19	2,3-Bornanedione	0.17%
20	Ethyl-4-dimethylamino-	
21	benzoate	4.30%

22

23 Again, the powder and liquid were mixed together  
 24 in a weight ratios varying from about 2:1 to about 3-1/2:1,  
 25 powder to liquid. Curing time was 30 seconds with a depth  
 26 of 5.50 mm when exposed to a visible light dental curing  
 27 unit. Diametral tensile strength was 6500 psi. The paste  
 28 had a workable time of 30 minutes under normal room  
 29 fluorescent lighting.

30

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1 EXAMPLE 8

2

3 Powder-Liquid System

4

5 Powder:

6 <u>Ingredients</u>	<u>Percentage by Weight</u>
7 Lithium aluminum silicate	66.80%
8 Barium glass	28.63%
9 Flint silica	2.84%
10 Benzoyl peroxide	0.20%
11 A-174 silane	1.51%
12 Glacial acetic acid	0.02%

13

14

15 Liquid

16 <u>Ingredients</u>	<u>Percentage by Weight</u>
17 Bis-GMA, i.e.,	
18 2,2'-propane-bis-	
19 [3-(4-phenoxy)-1,2-	
20 hydroxy propane-1-	
21 methacrylate]	57.40%
22 Triethylene glycol	
23 dimethacrylate	37.94
24 2,3-Bornanediol	0.02%
25 Ethyl-4-dimethylamino-	
26 benzoate	4.64%

27

28 Three parts of the powder and one part of the  
29 liquid were mixed together to form a paste. This paste,  
30 when exposed to a visible light dental curing unit for 30  
31 seconds, cured to a depth of 5.40 mm. Under normal room  
32 fluorescent lighting, the paste had a workable time of  
33 approximately 20 minutes. The diametral tensile strength  
34 was 6900 psi.

35

36

37

38

1 EXAMPLE 9

2

3 Powder-Liquid System

4

5 Powder:

6 Ingredients

Percentage by Weight

7	Lithium aluminum silicate	66.80%
8	Barium glass	28.63%
9	Flint silica	2.84%
10	Benzoyl peroxide	0.20%
11	A-174 silane	1.51%
12	Glacial acetic acid	0.02%

13

14

15 Liquid

16 Ingredients

Percentage by Weight

17	Ethoxylated bisphenol-A-	
18	dimethacrylate	75.98%
19	Triethylene glycol	
20	dimethacrylate	19.36%
21	2,3-Bornanediol	0.02%
22	Ethyl-4-dimethylamino-	
23	benzoate	4.64%

24

25 Three parts of the powder and one part of the liquid were  
 26 mixed together to form a paste. This paste, when exposed  
 27 to the output from a Visar dental visible light curing  
 28 unit for 30 seconds, cured to a depth of 5.30 mm. When  
 29 left exposed to room fluorescent lighting, the paste had a  
 30 working time of about 40 minutes and a diametral tensile  
 31 strength of 6940 psi.

32

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1 EXAMPLE 10

2 A comparison of curing of various powder/liquid  
3 systems utilizing different exciplex-forming photo-  
4 initiators

5  
6 A series of resin blends was prepared, all as  
7 indicated below as resins A-N, where all the percentages  
8 of ingredients are given by weight. Also a standard blend  
9 of powder was prepared. Benzoyl peroxide was added to the  
10 powder in different levels. The resultant powders were  
11 mixed with the resin blends and exposed to the output from  
12 a Visar dental curing light for 30 seconds, and the depth  
13 of cure measurement was taken.

14 As controls resin blends were made without one or  
15 all of the exciplex members.

16 On some of these samples, glass tubes 12 mm long  
17 were filled with the test material, and were wrapped with  
18 black vinyl tape to exclude light for 30 seconds, then the  
19 time was measured until the material at the opposite end  
20 of the tube was cured. This test will be referred to as  
21 the "Infinite Depth of Cure Test" in the following text.

22 As a control, a popular commercially available  
23 light-cured composite was tested in the same manner. It  
24 initially cured in 30 seconds to a depth of 3.05 mm, and  
25 there was no increase in cure depth when measured after 16  
26 hours.

27

28 Standard Blend of Powder

29

30	Barium glass	29.54%
31	Lithium aluminum silicate	68.96%
32	A-174 silane	1.48%
33	Glacial acetic acid	0.02%

34

35

36

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## 1 Resin A:

2	Ethoxylated bisphenol-A-	
3	dimethacrylate	100.00%

4  
5 Resin A was mixed in a ratio of 1:2 with a powder blend  
6 containing 0.61% added benzoyl peroxide. No cure was  
7 observed.

8

## 9 Resin B:

10	Ethoxylated bisphenol-A-	
11	dimethacrylate	95.53%
12	2,3-Bornanediol	0.17%
13	Ethyl-4-dimethylamino-	
14	benzoate	4.30%

15

16 Resin B was mixed in a ratio of 1:3 with powder blends  
17 containing 0.20 and 0.22% added benzoyl peroxide. The cure  
18 depths observed were both 5.50 mm. The time in minutes  
19 after light exposure for "infinite cure" of the blend made  
20 with the 0.22% added peroxide was 30.

21

## 22 Resin C:

23	Ethoxylated bisphenol-A-	
24	dimethacrylate	91.70%
25	Benzoin methyl ether	8.30%

26

27 Resin C was mixed in a ratio of 1:3 with a powder blend  
28 containing 0.20% added benzoyl peroxide. The cure depth  
29 was 1.32 mm. There was no subsequent increase in cure  
30 depth.

31

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## 1 Resin D:

2	Ethoxylated bisphenol-A-	
3	dimethacrylate	84.60%
4	Benzoin methyl ether	7.70%
5	Ethyl-4-dimethylamino-	
6	benzoate	7.70%

7  
8 Resin D was mixed in a ratio of 1:3 with a powder blend  
9 containing 0.20% added benzoyl peroxide. The cure depth  
10 was 2.55 mm. The time in minutes after light exposure for  
11 "infinite cure" of the blend was 60.

12

## 13 Resin E:

14	Ethoxylated bisphenol-A-	
15	dimethacrylate	82.30%
16	Benzoin methyl ether	7.70%
17	Ethyl-2-dimethylamino-	
18	benzoate	10.00

19

20 Resin E was mixed in a ratio of 1:3 with a powder blend  
21 containing 0.20% added benzoyl peroxide. The cure depth  
22 was 2.65 mm. The time in minutes after light exposure for  
23 "infinite cure" of the blend was 45.

24

## 25 Resin F:

26	Ethoxylated bisphenol-A-	
27	dimethacrylate	86.60%
28	Benzoin methyl ether	3.40%
29	Ethyl-2-dimethylamino-	
30	benzoate	10.00

31

32 Resin F was mixed in a ratio of 1:3 with a powder blend  
33 containing 0.20% added benzoyl peroxide. The cure depth  
34 was 2.74 mm. The time in minutes after light exposure for  
35 "infinite cure" of the blend was 60.

36

37

38

## 1 Resin G:

2	Ethoxylated bisphenol-A-	
3	dimethacrylate	88.80%
4	Benzoin methyl ether	3.50%
5	Ethyl-4-dimethylamino-	
6	benzoate	7.70%

7  
8 Resin G was mixed in a ratio of 1:3 with a powder blend  
9 containing 0.20% added benzoyl peroxide. The cure depth  
10 was 3.53 mm. The time in minutes after light exposure for  
11 "infinite cure" of the blend was 50.

12  
13 Resin H:

14	Ethoxylated bisphenol-A-	
15	dimethacrylate	91.70%
16	Benzil	8.30%

17  
18 Resin H was mixed in a ratio of 1:3 with a powder blend  
19 containing 0.20% added benzoyl peroxide. The cure depth  
20 was 4.06 mm. There was no subsequent increase in the depth  
21 of cure.

22  
23 Resin I:

24	Ethoxylated bisphenol-A-	
25	dimethacrylate	84.60%
26	Benzil	7.70%
27	Ethyl-4-dimethylamino-	
28	benzoate	7.70%

29  
30 Resin I was mixed in a ratio of 1:3 with a powder blend  
31 containing 0.20% added benzoyl peroxide. The cure depth  
32 was 4.84 mm. The time in minutes after light exposure for  
33 "infinite cure" of the blend was 25.

34  
35  
36  
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1 Resin J:

2	Ethoxylated bisphenol-A-	
3	dimethacrylate	84.60%
4	Benzil	7.70%
5	Ethyl-2-dimethylamino-	
6	benzoate	7.70%

7  
8 Resin J was mixed in a ratio of 1:3 with a powder blend  
9 containing 0.20% added benzoyl peroxide. The cure depth  
10 was 5.02 mm. The time in minutes after light exposure for  
11 "infinite cure" of the blend was 25.

12  
13 Resin K:

14	Ethoxylated bisphenol-A-	
15	dimethacrylate	91.50%
16	2,3-Bornanediene	0.17%
17	Ethyl-2-dimethylamino-	
18	benzoate	8.33%

19  
20 Resin K was mixed in a ratio of 1:3 with a powder blend  
21 containing 0.20% added benzoyl peroxide. The cure depth  
22 was 5.56 mm. The time in minutes after light exposure for  
23 "infinite cure" of the blend was 60.

24  
25 Resin L:

26	Ethoxylated bisphenol-A-	
27	dimethacrylate	88.80%
28	Dibenzyl ketone	3.40
29	Ethyl-4-dimethylamino-	
30	benzoate	7.80%

31  
32 Resin L was mixed in a ratio of 1:3 with a powder blend  
33 containing 0.20% added benzoyl peroxide. The cure depth  
34 was 1.87 mm. The time in minutes after light exposure for  
35 "infinite cure" of the blend was 45 minutes.

36  
37  
38

## 1 Resin M:

2	Ethoxylated bisphenol-A-	
3	dimethacrylate	86.60%
4	Dibenzyl ketone	3.40%
5	Ethyl-2-dimethylamino-	
6	benzoate	10.00%

7  
8 Resin M was mixed in a ratio of 1:3 with a powder blend  
9 containing 0.20% added benzoyl peroxide. The cure depth  
10 was 0.84 mm. The time in minutes after light exposure for  
11 "infinite cure" of the blend was 50 minutes.

12

## 13 Resin N:

14	Ethoxylated bisphenol-A-	
15	dimethacrylate	96.60%
16	Dibenzyl ketone	3.40%

17

18 Resin N was mixed in a ratio of 1:3 with a powder blend  
19 containing 0.20% added benzoyl peroxide. The cure depth  
20 was 1.55 mm. The time in minutes after light exposure for  
21 "infinite cure" of the blend was 52 minutes.

22

23

24 Paste-Paste Systems

25 Some dentists (and perhaps other users) prefer to  
26 work with pastes: most of these users also prefer to use  
27 equal amounts of the two pastes, so that paste-paste  
28 systems are usually formulated to enable use of equal  
29 amounts.

30 In general, the paste-paste system of the present  
31 invention may be formulated as follows:

32

33

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1 Paste A:

2		<u>Percentage by Weight</u>	
3	<u>Ingredients</u>		
4	Resin	14	to 39.63
5	Filler-colorant	84.68	to 59.46
6	Peroxide	0.10	to 0.75
7	A-174 silane	1.21	to 0.06
8	Butylated hydroxytoluene	0.01	to 0.10

10 Paste B:

11		<u>Percentage by Weight</u>	
12	<u>Ingredients</u>		
13	Resin	14	to 35.43
14	Filler-colorant	83.24	to 53.17
15	Exciplex forming	1.5	to 3.5
16	photoinitiator	1.21	to 0.05
17	A-174 silane	0.05	to 0.01
18	Glacial acetic acid		

19  
20 The two pastes are preferably mixed in equal  
21 amounts. Mixing time, working time, and setting time are  
22 approximately the same as for the powder-liquid systems,  
23 described above, and the results in cure and hardness are  
24 approximately the same, too. Again, ordinary room lighting  
25 has little curing effect. The resin may be the same in  
26 both pastes, as may the filler. The silane is preferably  
27 deposited on the filler of both pastes prior to making the  
28 pastes. The presence of both resin and peroxide in Paste A  
29 seems not to effect a cure nor to affect substantially the  
30 storage life.

31 More specifically considered, the paste-paste  
32 system employs the following formulations:

33

34

35

36

37

1	<u>Paste A:</u>		
2	<u>Ingredients</u>	<u>Percent by Weight</u>	
3	Bis-GMA	0	to 32
4	Ethoxylated bisphenol-A-dimethacrylate	0	to 40
5	Ethylene glycol dimethacrylate	0	to 24
6	Diethylene glycol dimethacrylate	0	to 24
7	Triethylene glycol dimethacrylate	0	to 24
8	Polyethylene glycol dimethacrylate	0	to 24
9	Barium glass	0	to 25
10	Lithium aluminum silicate	0	to 85
11	Flint silica	0	to 8.5
12	Borosilicate glass	0	to 85
13	Fumed synthetic silica	0	to 52
14	Quartz	0	to 85
15	Strontium glass	0	to 85
16	Titanium dioxide	0	to 0.13
17	Tinting agents (e.g., iron oxides)	0	to 4
18	A-174 Silane	0.06	to 1.21
19	Peroxide curing agent	0.10	to 0.75
20	Butylated hydroxy toluene	0.01	to 0.1
21			
22			
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38			

1 Paste B:

## 2 Ingredients

## Percent by Weight

3	Bis-GMA	0	to 32
4	Ethoxylated bisphenol-A-dimethacrylate	0	to 40
5	Ethylene glycol dimethacrylate	0	to 24
6	Diethylene glycol dimethacrylate	0	to 24
7	Triethylene glycol dimethacrylate	0	to 24
8	Polyethylene glycol dimethacrylate	0	to 24
9	Barium glass	0	to 25
10	Lithium aluminum silicate	0	to 85
11	Flint silica	0	to 8.5
12	Borosilicate glass	0	to 85
13	Fumed synthetic silica	0	to 52
14	Quartz	0	to 85
15	Strontium glass	0	to 85
16	Titanium dioxide	0	to 0.13
17	Tinting agents (e.g., iron oxides)	0	to 4
18	A-174 Silane	0.05	to 1.21
19	Exciplex-forming-photoinitiator	1.5	to 3.5
20	Glacial acetic acid	0.01	to 0.05

21

22           This formulation should be read with the more  
23 general one preceding it, to supply the percentages of  
24 fillers, resins, and silane needed, along with appropriate  
25 amounts of the curing agents. All percentages are by  
26 weight.

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1 EXAMPLE 112 Paste-Paste System

3

4 Paste A:5 Ingredients Percentage by Weight

6	Ethoxylated bisphenol-A-	
7	dimethacrylate	17.66%
8	Benzoyl peroxide	0.30%
9	Butylated hydroxytoluene	0.04%
10	Barium glass	24.25%
11	Lithium aluminum silicate	56.43%
12	Fumed silica	0.92%
13	A-174 silane	0.40%

14

15 The fumed silica may be Aerosil 200 of Degussa Corp. of  
16 Teterboro, New Jersey.

17

18 Paste B:19 Ingredients Percentage by Weight

20	Ethoxylated bisphenol-A-	
21	dimethacrylate	14.94%
22	2,3-Bornanediene	0.06%
23	Ethyl-4-dimethylamino	
24	benzoate	1.55%
25	Barium glass	24.394%
26	Lithium aluminum silicate	56.92%
27	Fumed silica	0.92%
28	A-174 silane	1.2%
29	Glacial acetic acid	0.016%

30

31 The two pastes are preferably mixed in equal  
32 quantities just before application and are cured by a  
33 dental curing light, such as Visar, or equivalent. When so  
34 mixed and exposed to a visible light curing unit for 30  
35 seconds, the material cured to a depth of 5.43 mm. The  
36 diametral tensile strength was 6990 psi.

37

38



1 EXAMPLE 12

2

3 Paste A:

4 <u>Ingredients</u>	<u>Percentage by Weight</u>
5 Ethoxylated bisphenol-A-	
6 dimethacrylate	17.66%
7 Benzoyl peroxide	0.30%
8 Butylated hydroxytoluene	0.04%
9 Strontium glass	79.88%
10 Fumed silica	0.92%
11 A-174 silane	1.20%

12

13

14 The strontium glass may be Ray-sorb T-4000 of  
15 Kimble Division of Owens-Illinois.

16

17 Paste B:

18 <u>Ingredients</u>	<u>Percentage by Weight</u>
19 Ethoxylated bisphenol-A-	
20 dimethacrylate	14.94%
21 2,3-Bornanediol	0.06%
22 Ethyl-4-dimethylamino	
23 benzoate	1.55%
24 Strontium glass	81.3284%
25 Fumed silica	0.92%
26 A-174 silane	1.20%
27 Glacial acetic acid	0.0016%

28

29 Equal or substantially equal amounts of pastes A  
30 and B are mixed together just before use. When so mixed  
31 and exposed to a visible light curing unit for 30 seconds,  
32 the material cured to a depth of 5.50 mm. The diametral  
33 tensile strength was 4790 psi.

34

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1 EXAMPLE 13

2           The pastes from Examples 11 and 12, mixed in equal  
3 parts, were exposed to the output from a Visar dental  
4 curing unit for 30 seconds. The samples were tested to  
5 determine the time required to achieve a 12 mm (or  
6 "infinite") depth of cure. The samples were tested as  
7 described previously. Pastes A and B of Example 11 when  
8 mixed together obtained "infinite" cure in 35 minutes.  
9 Pastes A and B of examples 12 when mixed together obtained  
10 "infinite" cure in 35 minutes.

11

12 Paste-Powder Systems

13           A third type of system is somewhat of a blend  
14 between the powder-liquid system and the paste-paste  
15 system. Here, the powder remains substantially the same as  
16 in the powder-liquid system, except that it has a larger  
17 percentage of peroxide. However, the paste contains the  
18 exciplex-forming members dissolved in a liquid resin, and  
19 the filler, suspended therein. This paste material should  
20 be stored in a light-free container. Typically, a black  
21 polyethylene or polypropylene syringe may be used as the  
22 container, as in the paste-paste systems.

23           The powder is coated with a suitable silane, such  
24 as gamma methacryloxy propyl trimethoxy silane, and has  
25 benzoyl peroxide dispersed over its surface. This  
26 component may be stored in a container suited to dispers-  
27 ing small amounts. A small cylindrical plastic vial with a  
28 small orificed dropper tip is preferred.

29           In practice, an amount of the paste is expressed  
30 onto a mixing pad, then a very small amount--1/10 to  
31 1/20-- of the powder is mixed in; so the powder has more  
32 peroxide in it than in previous systems discussed. The  
33 result is that the paste is thickened--a condition desired  
34 by some dentists--and also that depth of cure and cure  
35 efficiency are improved.

36           A general formulation may be expressed as follows:

37

38

1 Paste:

2	<u>Ingredients</u>	<u>Percentage by Weight</u>
3	Resin	13.00 to 63.4
4	Filler-colorant	84.78 to 32.85
5	Exciplex-forming	
6	photoinitiators	0.7 to 3.696
7	A-174 silane	1.50 to 0.05
8	Glacial acetic acid	0.02 to 0.004

10 Powder:

11	<u>Ingredients</u>	<u>Percentage by Weight</u>
12	Filler-colorant	99.58 to 83.83
13	A-174 silane	0.10 to 6
14	Peroxide	0.30 to 10.00
15	Glacial acetic acid	0.02 to 0.17

17 The mixture is preferably done in a ratio varying  
18 between 20 to 1 of paste to powder to 10 to 1 of paste to  
19 powder. More specifically, this system may comprise the  
20 following, with resin, filler, etc., ingredients always  
21 lying within the above-given ranges and percentages being  
22 by weight:

23

24

25

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1	<u>Paste:</u>		
2	<u>Ingredients</u>	<u>Percent by Weight</u>	
3	Bis-GMA	0	to 32
4	Ethoxylated bisphenol-A-		
5	dimethacrylate	0	to 63.4
6	Ethylene glycol dimethacrylate	0	to 24
7	Diethylene glycol dimethacrylate	0	to 24
8	Triethylene glycol dimethacrylate	0	to 24
9	Polyethylene glycol dimethacrylate	0	to 24
10	Barium glass	0	to 25
11	Lithium aluminum silicate	0	to 85
12	Flint silica		to 8.5
13	Borosilicate glass	0	to 85
14	Fumed synthetic silica	0	to 52
15	Strontium glass	0	to 85
16	Quartz	0	to 85
17	Titanium dioxide	0	to 0.13
18	Tinting agents (e.g., iron oxides)	0	to 4
19	A-174 Silane	0.05	to 1.25
20	Exciplex-forming photoinitiators	0.7	to 3.70
21	Glacial acetic acid	0.004	to 0.02
22			
23	<u>Powder:</u>		
24	<u>Ingredients</u>	<u>Percent by Weight</u>	
25			
26	Barium glass	0	to 30
27	Lithium aluminum silicate	0	to 99.65
28	Flint silica	0	to 10
29	Borosilicate glass	0	to 99.65
30	Fumed synthetic silica	0	to 99.65
31	Strontium glass	0	to 99.65
32	Titanium dioxide	0	to 0.15
33	Tinting agent (e.g., iron oxides)	0	to 5
34	A-174 silane	0	to 6.0
35	Peroxide curing agent		
36	(e.g. benzoyl peroxide)	0.30	to 10
37	Glacial acetic acid	0.02	to 0.17
38			

1 EXAMPLE 142 Paste-Powder System3  
4 Paste:

5	<u>Ingredients</u>	<u>Percentage by Weight</u>
6	Ethoxylated bisphenol-A-	
7	dimethacrylate	63.40%
8	2,3-Bornanediol	0.056%
9	Ethyl-4-dimethylamino	
10	benzoate	3.1%
11	Fumed silica	16.05%
12	Barium glass	16.59%
13	Titanium dioxide	00.05%
14	Yellow iron oxide	00.16%
15	Butylated hydroxytoluene	0.005%
16	Glacial acetic acid	0.004%
17	2-Hydroxy-4-methoxy	
18	benzophenone	0.585%

19  
20 Powder:

21	<u>Ingredients</u>	<u>Percentage by Weight</u>
22	Fumed silica	86.07%
23	Benzoyl peroxide	8.60%
24	A-174 silane	5.16%
25	Acetic acid	0.17%

26  
27 When a small amount (10% by weight) of the powder  
28 is added to the paste, the resulting heavy paste has a  
29 working time of over 20 minutes. When so mixed and exposed  
30 to the Visar curing light for 30 seconds, the depth of  
31 cure measured at least 4.50 mm. Diametral tensile strength  
32 was 5000 psi.

33

34

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1 EXAMPLE 152 Paste-Powder System

3

4

Paste:

5

IngredientsPercentage by Weight

6

Bis-GMA

9.74%

7

Triethylene glycol

8

dimethacrylate

6.49%

9

2,3-Bornanediol

0.03%

10

Ethyl-4-dimethylamino

11

benzoate

0.76%

12

Barium glass

24.52%

13

Lithium aluminum silicate

57.21%

14

A-174 silane

1.23%

15

Glacial acetic acid

0.02%

16

17

Powder:

18

IngredientsPercentage by Weight

19

Barium glass

29.05%

20

Lithium aluminum silicate

67.78%

21

A-174 silane

1.45%

22

Benzoyl peroxide

1.696%

23

Glacial acetic acid

0.024%

24

25

26 The paste and powder are mixed at a weight ratio  
27 of 100:5, paste:powder. When so mixed and exposed to a  
28 Visar curing unit for 30 seconds, the depth of cure was  
29 5.40 mm. The time to obtain a 12 mm cure was 25 minutes.  
30 The diametral tensile strength was 7090 psi.

31

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1 EXAMPLE 162 Paste-Powder System

3

4 Paste:5 IngredientsPercentage by Weight

6	Ethoxylated bisphenol-A-	
7	dimethacrylate	12.98%
8	Triethylene glycol	
9	dimethacrylate	3.25%
10	2,3-Bornanediol	0.03%
11	Ethyl-4-dimethylamino	
12	benzoate	0.76%
13	Barium glass	24.52%
14	Lithium aluminum silicate	57.21%
15	A-174 silane	1.23%
16	Glacial acetic acid	0.02%

17

18 Powder:19 IngredientsPercentage by Weight

20	Barium glass	29.05%
21	Lithium aluminum silicate	67.78%
22	A-174 silane	1.45%
23	Benzoyl peroxide	1.696%
24	Glacial acetic acid	0.024%

25

26 The paste and powder are mixed together at a  
27 weight ratio of 100:5, paste:powder. When so mixed and  
28 exposed to the output from a Visar curing unit for 30  
29 seconds, the depth of cure was 5.15 mm. The time to a 12  
30 mm cure was 35 minutes. The diametral tensile strength was  
31 5250 psi.

32

33 Gel-Powder Systems

34 Using powder like that used in the powder-liquid  
35 system but employing a gel instead of a liquid, a general  
36 formulation for these systems may be as follows:

37

38

1	<u>Gel:</u>	
2	<u>Ingredients</u>	<u>Percentage by Weight</u>
3	Resin	49 to 80.4
4	Filler	49 to 10.3
5	A-174 silane	0 to 1.25
6	Exciplex-forming	
7	photoinitiator	2 to 8
8	Glacial acetic acid	0 to 0.05

9		
10	<u>Powder:</u>	
11	<u>Ingredients</u>	<u>Percentage by Weight</u>
12	Filler	99.95 to 93.786
13	A-174 silane	0 to 1.50
14	Peroxide	0.05 to 4.69
15	Glacial acetic acid	0 to 0.024
16		

17 The mixture may vary from about one part of powder  
18 to twenty parts of gel to about three parts of powder to  
19 one part of gel.

20 More specifically, while adhering to the general  
21 formulation above, the system may use individual  
22 ingredients as follows:

23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38



- 40 -

1 Gel:2 IngredientsPercent by Weight

3		
4	Bis-GMA	0 to 72
5	Ethoxylated bisphenol-A-dimethacrylate	0 to 90
6	Ethylene glycol dimethacrylate	0 to 54
7	Diethylene glycol dimethacrylate	0 to 54
8	Triethylene glycol dimethacrylate	0 to 54
9	Polyethylene glycol dimethacrylate	0 to 54
10	Barium glass	0 to 15
11	Lithium aluminum silicate	0 to 50
12	Flint silica	to 5.
13	Borosilicate glass	0 to 50
14	Fumed synthetic silica	0 to 50
15	Strontium glass	0 to 50
16	Quartz	0 to 50
17	Titanium dioxide	0 to 1
18	Tinting agents (e.g., iron oxides)	0 to 5
19	A-174 Silane	0 to 1.25
20	Exciplex-forming photoinitiators	2 to 8
21	Glacial acetic acid	0 to 0.05

23 Powder:24 IngredientsPercent by Weight

25		
26	Barium glass	0 to 30
27	Lithium aluminum silicate	0 to 99.95
28	Flint silica	0 to 10
29	Borosilicate glass	0 to 99.95
30	Fumed synthetic silica	0 to 99.95
31	Strontium glass	0 to 99.95
32	Titanium dioxide	0 to 1.50
33	Tinting agent (e.g., iron oxides)	0 to 5
34	A-174 silane	0 to 1.50
35	Peroxide curing agent	
36	(e.g. benzoyl peroxide)	0.05 to 4.69

1 EXAMPLE 172 Gel-Powder System

3

4 Gel:5 IngredientsPercentage by Weight

6

7

Ethoxylated bisphenol-A-

8

dimethacrylate

76.40%

9

2,3-Bornanediol

0.06%

10

Ethyl-4-dimethylamino

11

benzoate

2.28%

12

Fumed silica

8.30%

13

Barium glass

3.831%

14

Lithium aluminum silicate

8.938%

15

A-174 silane

0.188%

16

Glacial acetic acid

0.003%

17

18 Powder:

19 The powder is the same as that of Example 16. The  
20 powder and gel are mixed together in a weight ratio of  
21 3:1, powder to gel. When exposed to a visible light dental  
22 curing unit for 30 seconds, the material cured to a depth  
23 of 4.90 mm. Under normal room fluorescent lighting, the  
24 paste had a workable time of approximately 35 minutes. The  
25 diametral tensile strength was 5800 psi.

26

27 EXAMPLE 1828 Gel-Powder System

29

30 Gel:31 IngredientsPercentage by Weight

32

Ethoxylated bisphenol-A-

33

dimethacrylate

76.34%

34

2,3-Bornanediol

0.14%

35

Ethyl-4-dimethylamino

36

benzoate

2.28%

37

Fumed silica

21.24%

38

1           Powder:

2           The powder is the same as that used in example 16  
3 The powder and gel are mixed in a ratio of 3:1, powder to  
4 gel. When, exposed to a visible light dental curing unit  
5 30 seconds, the material cured to a depth of 5.40 mm.  
6 Under normal fluorescent lighting, the paste has a  
7 workable time of 25 minutes. The diametral tensile  
8 strength was 7090 psi.

9  
10           This restorative system may be used in the repair  
11 of fractured porcelain material, natural teeth, or in any  
12 other intra-oral situation where a resin material is  
13 desired to replace or simulate tooth structure that is  
14 capable of being polymerized by visible light and having  
15 the process continue after the light is removed.

16           Also, this restorative system, which is essenti-  
17 ally a light-cured system, achieves uniform polymerization  
18 within thirty minutes to one hour after insertion in the  
19 patient's mouth, even though variable amounts of light be  
20 exposed to the polymerizing resin.

21           This system eliminates the color changes that tend  
22 to occur when certain resins mixed with curing resins are  
23 exposed to ultra-violet or visible light.

24           To those skilled in the art to which this  
25 invention relates, many changes in construction and widely  
26 differing embodiments and applications of the invention  
27 will suggest themselves without departing from the spirit  
28 and scope of the invention. The disclosures and the  
29 descriptions herein are purely illustrative and are not  
30 intended to be in any sense limiting.

31           What is claimed is:

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- 1           1. A filled-resin composition useful for porcelain  
2 repair and as a dental composite and therefore made up of  
3 non-toxic materials, comprising:
  - 4           a methacrylate functional resin usable in dental  
5 composites,  
6           powdered filler-colorant therein,  
7           at least one photoinitiator for said resin in an  
8 amount sufficient to initiate polymerization and complete  
9 it in depth within about half a minute when exposed to a  
10 visible-light output of at least 5,000 foot candles, said  
11 photoinitiator being an exciplex of (1) either  
12 2,3-bornanedione or benzil and (2) either ethyl-4-dimethyl  
13 amino benzoate or ethyl-2-dimethyl amino benzoate, and  
14           at least one accelerator-free peroxide curing  
15 agent for said resin in an effective amount for completing  
16 polymerization within about an hour of any portion of said  
17 resin not receiving sufficient light to effectuate  
18 complete cure before then.
- 19  
20           2. The composition of claim 1 wherein said photo-  
21 initiator is 2,3-bornanedione with ethyl-4-dimethyl amino  
22 benzoate.  
23
- 24           3. The composition of claim 1 wherein said photo-  
25 initiator is 2,3-bornanedione with ethyl-2-dimethyl amino  
26 benzoate.  
27
- 28           4. The composition of claim 1 wherein said photo-  
29 initiator is benzil with ethyl-4-dimethyl amino benzoate.  
30
- 31           5. The composition of claim 1 wherein said photo-  
32 initiator is benzil with ethyl-2-dimethyl amino benzoate.  
33  
34  
35  
36  
37  
38

- 1           6. A two-part system for making a filled  
2 methacrylate-functional resin composition by mixture of  
3 the two parts, comprising:  
4           first part: dental-type filler powder with an  
5 accelerator-free peroxide curing agent for said resin,  
6           second part: dental-type methacrylate-functional  
7 resin with photoinitiator therefor,  
8           said photoinitiator being an exciplex of (1)  
9 either 2,3-bornanedione or benzil and (2) either ethyl-  
10 4-dimethyl amino benzoate or ethyl-2-dimethyl amino  
11 benzoate, in an amount sufficient to initiate  
12 polymerization and complete it within about half a minute  
13 after the first part and second parts are mixed and then  
14 exposed during cure to at least 5,000 foot candles visible  
15 light,  
16           said peroxide curing agent being present in an  
17 amount effective to complete cure of any resin portion not  
18 sufficiently exposed to said light within about an hour.  
19  
20           7. The system of claim 6 wherein the first part is  
21 in the form of a powder.  
22  
23           8. The system of claim 7 wherein the second part  
24 is in the form of a liquid.  
25  
26           9. The system of claim 8 wherein the powder to  
27 liquid weight ratio is from about 1:1 to about 4:1.  
28  
29           10. The system of claim 7 wherein the second part  
30 is in the form of a gel and also contains some filler.  
31  
32           11. The system of claim 10 wherein the powder-gel  
33 weight ratio is from about 1:20 to about 3:1.  
34  
35           12. The system of claim 6 wherein both the first  
36 and second parts are in paste form, both containing  
37 substantial amounts of filler.  
38

1           13. The system of claim 12 wherein the first and  
2 second parts are so formulated to enable mixture of equal  
3 parts by weight at the time of use.

4

5           14. A porcelain-repair and dental composite  
6 composition of matter consisting essentially of  
7           a powder component consisting essentially by  
8 weight of:

9

10	Dental filler-colorant material	99.85% to 97.7%
11	Gamma-methacryloxy propyl	
12	trimethoxy silane	0.10% to 1.55%
13	Peroxide curing agent	0.05% to 0.70%
14	Glacial acetic acid	0 to 0.05%

15

16 and a liquid component consisting essentially, by weight  
17 of:

18	a methacrylate-functional resin	
19	suitable for use in dental	
20	composites	99.3% to 82%
21	exciplex-forming photoinitiator	
22	for said resin	0.7% to 18%

23

24 said photoinitiator an exciplex of either (1) 2,3-  
25 bornanediol or benzil and (2) either ethyl-4-dimethyl  
26 amino benzoate or ethyl-2-dimethyl amino benzoate, and  
27 said powder and resin being mixed together in a weight  
28 ratio between 1:1 and 4:1 of powder to liquid.

29

30           15. The porcelain-repair and dental composite  
31 composition of matter of claim 14 wherein:

32           said filler-colorant consists essentially by  
33 weight of ingredients totaling as in claim 14 and selected  
34 from the group consisting of:

35

36

37

38

1	Barium glass	0% to 30%
2	Lithium aluminum silicate	0% to 99.85%
3	Flint silica	0% to 10%
4	Borosilicate glass	0% to 99.85%
5	Fumed synthetic silica	0% to 99.85%
6	Quartz	0% to 99.85%
7	Custer feldspar	0% to 10%

8  
9       said powder component also including, in addition  
10 to the silane, the peroxide curing agent, and the glacial  
11 acetic acid:

12		
13	Titanium dioxide	0% to 0.15%
14	Metal salts	0% to 5.00%

15  
16       said methacrylate-functional resin totaling as in  
17 claim 14 and consisting essentially by weight of  
18 ingredients:

19		
20	Bis-GMA	0% to 80%
21	Ethoxylated bisphenol-A-	
22	dimethacrylate	0% to 99%
23	Ethylene glycol dimethacrylate	0% to 60%
24	Diethylene glycol dimethacrylate	0% to 60%
25	Triethylene glycol dimethacrylate	0% to 60%
26	Polyethylene glycol dimethacrylate	0% to 60%
27	Exciplex forming photoinitiator	0.7% to 18%

28  
29       16. The composition or system of any one of claims  
30 1, 6, and 14 wherein said peroxide curing agent is benzoyl  
31 peroxide.

32  
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38

1 17. A porcelain-repair and dental composite  
2 restorative material consisting essentially of:

3 (a) a powder component, consisting essentially of a  
4 powdered dental filler-colorant, with a  
5 powdered peroxide curing agent in an amount  
6 between 0.05% and 1% by weight of said powder  
7 component, and

8 (b) a liquid component, consisting essentially of  
9 (1) a methacrylate-functional resin suitable  
10 for use in dental composites in an amount  
11 of 84-96% by weight of said liquid  
12 component, and

13 (2) a photoinitiator for said resin consist-  
14 ing of an exciplex incorporating as one  
15 ingredient either ethyl-4-dimethyl amino  
16 benzoate or ethyl-2-dimethyl amino  
17 benzoate in an amount of about 0.7 to 10%  
18 by weight of said liquid component, the  
19 other ingredient being either 2,3-  
20 bornanediene or benzil and present in an  
21 amount of 0.01 - 8%, by weight of said  
22 liquid component, for a total photoiniti-  
23 ator amount by weight of said liquid  
24 component of about 0.7 to 18%,

25 said powder and liquid components being mixed  
26 together just before use in a weight ratio of from 2:1 to  
27 3-1/2 powder to liquid.

28

29 18. The restorative material of claim 17, wherein  
30 said powder component, by weight of said powder component  
31 contains:

32 Barium glass	23 - 30%
33 Lithium aluminum silicate	54 - 70%
34 Flint silica	1 - 70%

35

36 for a total filler content of about 97-1/2 to  
37 99.85%.

38



1 19. The restorative material of claim 17 wherein  
2 said powder component also contains glacial acetic acid  
3 and gamma-methacryloxy propyl trimethoxy silane.  
4

5 20. The restorative material of claim 17 wherein  
6 said glacial acetic acid is present in an amount of about  
7 0.001 - 0.05%, by weight of said powder component, and  
8 said silane is present in an amount of about 1/10 of 1% to  
9 about 1-1/2% by weight of said powder component.  
10

11 21. The restorative material of claim 17 wherein  
12 said resin is ethoxylated bisphenol-A-dimethacrylate in an  
13 amount of about 82 to 99.3% by weight of said liquid  
14 component.  
15

16 22. The restorative material of claim 17 wherein  
17 said resin is a mixture, by weight of said liquid  
18 component, of about 60-84% ethoxylated bisphenol-A-  
19 dimethacrylate and about 40-16% triethylene glycol  
20 dimethacrylate.  
21

22 23. The restorative material of claim 17 wherein  
23 said resin is a mixture, by weight of said liquid  
24 component, of about 55% Bis-GMA and about 36% of  
25 triethanol glycol dimethacrylate.  
26

27 24. The restorative material of claim 17 employing  
28 2,3-bornanedione in amounts by weight of said liquid  
29 component of 0.02 - 0.2%.  
30

31 25. The restorative material of claim 17 wherein  
32 said liquid component also includes BHT in an amount of  
33 about 0.02% by weight of said liquid component.  
34  
35  
36  
37  
38

1           26. A two-paste system for porcelain and dental  
2 restoration, said pastes being mixed together at the time  
3 of use in substantially equal amounts by weight,

4           both pastes containing methacrylate-functional  
5 resin suitable for use in dental components and dental  
6 filler material an an amount totaling over 95% thereof by  
7 weight of each paste,

8           one said paste containing a peroxide curing agent  
9 for said resin in an amount of about 0.1% to 1.0% by  
10 weight of that paste,

11          the other said paste containing an exciplex  
12 visible-light-reactive photoinitiator for said resin in  
13 an amount of about 1 to 3.5% by weight of that paste, said  
14 exciplex being a mixture of (1) either 2,3-bornanedione or  
15 benzil and (2) either ethyl-4-dimethyl amino benzoate or  
16 ethyl-2-dimethyl amino benzoate.

17  
18          27. The system of claim 26 in which each paste  
19 also contains gamma-methacryloxy propyl trimethoxy silane  
20 in an amount of about 0.05 to 1.2% by weight of each  
21 paste.

22  
23          28. The system of claim 26 in which at least one  
24 of the pastes also contains glacial acetic acid in an  
25 amount of at least 0.0015% by weight of that paste.

26  
27          29. The system of claim 26 wherein said resin is  
28 ethoxylated bisphenol-A-dimethacrylate.

29  
30          30. The system of claim 26 wherein said resin is  
31 present in the peroxide-containing paste in an amount of  
32 about 14 - 40% and is present in the exciplex-containing  
33 paste in an amount of 14-36%.

34  
35  
36  
37  
38

1           31. The system of claim 26 wherein said filler is  
2 chosen from (a) the group consisting of strontium glass  
3 and a mixture of barium glass with lithium aluminum  
4 silicate, and also includes fumed silica.

5  
6           32. The system of claim 31 wherein the filler  
7 comprises, by weight of each paste about 1% of fumed  
8 silica and about 80% of strontium glass.

9  
10          33. The system of claim 31 wherein the filler  
11 comprises, by weight of each paste, about 1% of fumed  
12 silica, about 23-25% of barium glass, and about 54-58% of  
13 lithium aluminum silicate.

14  
15          34. A paste-powder system for use in dental and  
16 porcelain restoration, the paste and powder being mixed at  
17 the time of use at a ratio of paste to powder of about  
18 10:1 to 20:1,

19           said paste comprising the mixture of methacrylate-  
20 functional dental resin and powdered dental filler in a  
21 total amount of about 96-99% by weight of the paste and  
22 having an exciplex, visual-light reactive photoinitiator,

23           said powder consisting essentially of a dental  
24 filler and a peroxide curing agent for the resin in an  
25 amount of about 0.3% - 9% of the powder,

26           said exciplex being made up of

27           (a) 2,3-bornanedione in an amount of about 0.03%  
28 to 0.06% by weight of said paste and,

29           (b) either ethyl-4-dimethyl amino benzoate or  
30 ethyl-2-dimethyl amino benzoate in an amount of about 0.75  
31 to 3.25% by weight of said paste.

32

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1           35. The system of any of claims 1, 6, 17 and 34  
2 wherein said resin is selected from the group consisting  
3 of ethoxylated bisphenol-A-dimethacrylate, bis-GMA a  
4 mixture thereof with an ethylene glycol dimethacrylate,  
5 and a mixture of bis-GMA with an ethylene glycol  
6 dimethacrylate.

7  
8           36. The system of claim 34 wherein the resin is  
9 from 16-64% ethoxylated bisphenol-A-dimethacrylate, by  
10 weight of said paste.

11  
12           37. The system of claim 34 wherein the resin is a  
13 mixture of about 13% ethoxylated bisphenol-A-  
14 dimethacrylate and about 3-1/4% of triethylene glycol  
15 dimethacrylate, both by weight of said resin.

16  
17           38. The system of claim 34 wherein the resin is a  
18 mixture of about 10% bis-GMA and about 6-1/2% triethylene  
19 glycol dimethacrylate, both by weight of said resin.

20  
21           39. The system of claim 34 wherein at least the  
22 powder contains gamma-methacryloxy propyl trimethoxy  
23 silane, in an amount of about 1.25 to 5.25% by weight of  
24 its component.

25  
26           40. The system of claim 34 wherein at least the  
27 powder contains glacial acetic acid in an amount of about  
28 0.02 to 0.2% by weight of its component.

29  
30           41. A gel-powder system for use in dental and  
31 porcelain restoration, the gel and powder being mixed at  
32 the time of use for cure by visible light, in a ratio of  
33 about 20:1 to 1:3 of gel to powder,

34           the gel consisting essentially of about 3/4  
35 methacrylate-functional dental resin and about 1/4 dental  
36 filler to a total amount of about 93-98% by weight of said  
37 gel and an exciplex, visible-light-reactive photoiniti-  
38

1 ator having two ingredients, one of which is either ethyl-  
2 4-dimethyl amino benzoate or ethyl-2-dimethyl amino  
3 benzoate,

4 said powder consisting essentially of a dental  
5 filler and an accelerator-free peroxide curing agent for  
6 said resin in an amount of about 0.1% - 10% by weight of  
7 said powder,

8 said exciplex being made up of

9 (a) 2,3-bornanediol in an amount of about 0.005  
10 to 0.15% by weight of said gel and,

11 ~~(b) either ethyl-4-dimethyl amino benzoate or~~  
12 ~~ethyl-2-dimethyl amino benzoate in an amount of about 2.0~~  
13 ~~to 8% by weight of said gel.~~

14

15 42. The system of claim 41 wherein said resin is  
16 ethoxylated bisphenol-A-dimethacrylate.

17

18 43. The system or material of claim 17 or claim 41  
19 wherein said filler for the powder component is selected  
20 from the group consisting of barium glass, strontium  
21 glass, lithium aluminum silicate, flint silica and  
22 mixtures of the members of this group with each others.

23

24 44. The system or material of claim 41 wherein  
25 said filler for the powder component is a mixture of  
26 barium glass, lithium aluminum silicate and flint silica.

27

28 45. The system of claim 41 wherein said filler for  
29 the powder component contains, by weight of the powder,  
30 26-30% barium glass, 62-70% lithium aluminum silicate and  
31 1-10% flint silica.

32

33 46. The system of claim 34 or claim 41 wherein  
34 said filler for the gel component is fumed silica.

35

36

37

38

1           47. The system of claim 34 or claim 41 wherein  
2 said filler for the gel component is a mixture of barium  
3 glass and lithium aluminum silicate.  
4

5           48. The system of claim 41 wherein said filler for  
6 the gel component comprises, by weight of the gel, about  
7 2-5% barium glass, about 5-10% lithium aluminum silicate  
8 and about 7-10% fumed silica.  
9

10          49. The system of claim 41 wherein at least the  
11 powder component contains gamma-methacryloxy propyl  
12 trimethoxy silane, in an amount of about 0.05 to 2.0% by  
13 weight of its component.  
14

15          50. The system of claim 41 wherein at least the  
16 powder component contains glacial acetic acid, in an  
17 amount of about 0.01 to 0.05% by weight of its component.  
18

19          51. A method for repairing porcelain or teeth,  
20 comprising

21           mixing together under ordinary indoor lighting  
22 conditions, a methacrylate functional resin usable in  
23 dental composites, powdered dental filler-colorant, at  
24 least one photoinitiator for said resin in an amount  
25 sufficient to initiate polymerization and complete it in  
26 depth within about half a minute when exposed to a  
27 visible-light output of at least 5000 foot-candles, said  
28 photoinitiator being an exciplex of (1) either  
29 2,3-bornanedione or benzil and (2) either ethyl-4-dimethyl  
30 amino benzoate or ethyl-2-dimethyl amino benzoate, and at  
31 least one accelerator-free peroxide curing agent for said  
32 resin in an effective amount for completing polymerization  
33 within about an hour of any portion of said resin not  
34 receiving sufficient light to effect complete cure before  
35 then,

36           emplacing the mixture within a few minutes of the  
37 mixing, and  
38

1        curing at least a substantial portion of the  
2        emplaced mixture in situ for one half-minute under intense  
3        visual-light illumination of at least 5000 foot-candles,  
4        any resin then uncured by light being cured within about  
5        another hour by said peroxide curing agent.

6  
7        52. The method of claim 51 wherein the resin is at  
8        least one resin chosen from the group consisting of  
9        ethoxylated bisphenol-A-dimethacrylate, bis-GMA, and an  
10        adduct of 2,2'-propane bis [3-(4-phenoxy)-1, 2-hydroxy  
11        propane-1 methacrylate] and mono- or di- isocyanate.

12  
13        53. A method for preparing a storable filled-resin  
14        composition useful for porcelain repair and as a dental  
15        composite, comprising:

16        mixing a methacrylate functional resin usable in  
17        dental composites with at least one photoinitiator for  
18        said resin, in an amount sufficient to initiate polymeri-  
19        zation and complete it in depth within about half a minute  
20        when exposed to a visible-light output of at least 5000  
21        foot-candles, said photoinitiator being an exciplex of (1)  
22        either 2,3-bornanedione or benzil and (2) either ethyl-4-  
23        dimethyl amino benzoate or ethyl-2-dimethyl amino  
24        benzoate,

25        storing the resin-photoinitiator mixture in an  
26        opaque container,

27        coating a powdered dental filler-colorant with at  
28        least one accelerator-free peroxide curing agent for said  
29        resin in an effective amount substantially less than  
30        stoichiometric, and sufficient to effect completion of  
31        polymerization within about an hour of any portion of said  
32        resin not receiving sufficient light during said half a  
33        minute,

34        storing said filler-colorant and peroxide mixture,  
35        and

36  
37  
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1           at the time of use, mixing said resin-  
2 photoinitiator mixture with said peroxide-coated filler-  
3 colorant under ordinary indoor illumination.  
4

5           54. A method for repairing porcelain or teeth,  
6 comprising

7           preparing under ordinary indoor lighting  
8 conditions, a liquid mixture consisting essentially of a  
9 methacrylate functional resin usable in dental composites,  
10 and at least one photoinitiator for said resin in an  
11 amount sufficient to initiate polymerization and complete  
12 it in depth within about half a minute when exposed to a  
13 visible-light output of at least 5000 foot-candles, said  
14 photoinitiator being an exciplex of (1) either 2,3-  
15 bornanedione or benzil and (2) either ethyl-4-dimethyl  
16 amino benzoate or ethyl-2-dimethyl amino benzoate,

17           preparing under ordinary indoor lighting  
18 conditions a powdered mixture of powdered dental filler-  
19 colorant and at least one accelerator-free peroxide curing  
20 agent for said resin in an effective amount for completing  
21 polymerization within about an hour of any portion of said  
22 resin not receiving sufficient light to effect complete  
23 cure before then,

24           mixing said powder mixture and said liquid mixture  
25 together under ordinary indoor lighting conditions in a  
26 powder to liquid ratios of about 1:1 to 4:1 just prior to  
27 use to provide a repair mixture,

28           emplacing the repair mixture within a few minutes  
29 of the mixing, and

30           curing at least a substantial portion of the  
31 emplaced mixture in situ for one half-minute under intense  
32 visual-light illumination of at least 5000 foot-candles,  
33 any resin then uncured by light being cured within the  
34 next half hour by said peroxide curing agent.  
35  
36  
37  
38



1           55. The method of claim 54 wherein said exciplex  
2 constitutes about 0.7% to about 18% by weight of said  
3 liquid mixture and said peroxide constitutes about 0.1 to  
4 about 0.8% of said powder mixture.

5  
6           56. The method of claim 54 having the step in  
7 between preparing and mixing of storing said powder in a  
8 container and of storing said liquid in an opaque  
9 container.

10  
11           57. A method for repairing porcelain or teeth,  
12 comprising:

13           providing under ordinary indoor lighting  
14 conditions first paste consisting essentially of a  
15 methacrylate functional resin usable in dental composites,  
16 a powdered dental filler-colorant, and at least one photo-  
17 initiator for said resin in an amount sufficient to  
18 initiate polymerization and complete it in depth within  
19 about half a minute when exposed to a visible-light output  
20 of at least 5000 foot-candles, said photoinitiator being  
21 an exciplex of (1) either 2,3-bornanedione or benzil and  
22 (2) either ethyl-4-dimethyl amino benzoate or ethyl-2-  
23 dimethyl amino benzoate,

24           providing a under ordinary indoor lighting  
25 conditions second paste consisting essentially of a  
26 methacrylate functional resin usable in dental composites,  
27 a powdered dental filler colorant, and at least one  
28 accelerator-free peroxide curing agent for said resin in  
29 an effective amount for completing polymerization within  
30 about an hour of any portion of said resin not receiving  
31 sufficient light to effective complete cure before then,

32           mixing under ordinary indoor lighting conditions  
33 said first and second pastes in approximately the same  
34 amount of each, to form a paste mixture,

35           emplacing the paste mixture within a few minutes  
36 of the mixing, and

37

38

1           curing at least a substantial portion of the  
2   emplaced mixture in situ for one half-minute under intense  
3   visual-light illumination of at least 5000 foot-candles,  
4   any resin then uncured by light being cured within about  
5   an hour thereafter by said peroxide curing agent.

6  
7           58. The method of claim 57 wherein said first  
8   paste, at least, is prepared long in advance and compris-  
9   ing the step of storing said first paste in an opaque  
10   container until said mixing step.

11  
12           59. The method of claim 57 in which said exciplex  
13   constitutes about 1 to 4% by weight of said first paste  
14   and said peroxide constitutes about 0.1 to 1.0% by weight  
15   of said second paste.

16  
17           60. A method for repairing porcelain or teeth,  
18   comprising:

19           mixing together under ordinary indoor lighting  
20   conditions a paste consisting essentially of a methacry-  
21   late functional resin usable in dental composites,  
22   powdered dental filler-colorant, at least one photoiniti-  
23   ator for said resin in an amount sufficient to initiate  
24   polymerization and complete it in depth within about half  
25   a minute when exposed to a visible-light output of at  
26   least 5000 foot-candles, said photoinitiator being an  
27   exciplex of (1) an aromatic ketone or acetal and (2)  
28   either ethyl-4-dimethyl amino benzoate or ethyl-2-dimethyl  
29   amino benzoate,

30           mixing together under ordinary indoor lighting  
31   conditions a powder consisting essentially of a powdered  
32   dental filler-colorant and at least one accelerator-free  
33   peroxide curing agent for said resin in an effective  
34   amount for completing polymerization within about one-half  
35   hour of any portion of said resin not receiving sufficient  
36   light to effectively complete cure before then,

37  
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1 mixing together under ordinary indoor lighting  
2 conditions, immediately before use, said paste and said  
3 powder in a ratio of paste to powder of about 20:1 to  
4 10:1, to form a thick paste,

5 emplacing the thick paste within a few minutes of  
6 the mixing, and

7 curing at least a substantial portion of the  
8 emplaced mixture in situ for one half-minute under intense  
9 visual-light illumination of at least 5000 foot-candles,  
10 any resin then uncured by light being cured within about  
11 an hour thereafter by said peroxide curing agent.

12  
13 61. The method of any of claims 51, 53, 54, 57, or  
14 60 wherein said peroxide curing agent is benzoyl  
15 peroxide.

16  
17 62. The method of claim 60 wherein said mixing of  
18 said paste is done well in advance of use including the  
19 step of storing said paste in an opaque container prior to  
20 said mixing of the powder with the pad.

21  
22 63. The method of claim 60 wherein said exciplex  
23 constitutes about 0.7 to 4% of said paste and said  
24 peroxide constitutes about 0.3 to about 10% of said  
25 powder.

26  
27 64. A method for repairing porcelain or teeth,  
28 comprising:

29 mixing together under ordinary indoor lighting  
30 conditions,

31 a gel consisting essentially of about 3/4  
32 methacrylate-functional dental resin and about 1/4 dental  
33 filler to a total amount of about 93 to 97-1/2% by weight  
34 of the gel and an exciplex, visible-light-reactive photo-  
35 initiator having two ingredients, one of which is either

36

37

38

1 ethyl-4-dimethyl amino benzoate or ethyl-2-dimethyl amino  
2 benzoate, in a total amount of about 2% to 8% by weight of  
3 the gel,

4 with a powder consisting essentially of a filler  
5 and an accelerator free peroxide curing agent for the  
6 resin in an amount of about 0.1 - 5% by weight of the  
7 powder,

8 in a ratio of about 20:1 to 1:3 of gel to powder.  
9

10 65. The method of claim 64 wherein the resin is  
11 ethoxylated bisphenol-A-dimethacrylate.  
12

13 66. The method of claim 64 wherein the filler for  
14 the gel component is fumed silica.  
15

16 67. The method of claim 64 wherein the filler for  
17 the gel component comprises, by weight of the gel, about  
18 2-5% barium glass, about 5-10% lithium aluminum silicate  
19 and about 7-10% fumed silica.  
20

21 68. The method of claim 64 wherein the exciplex is  
22 made up of

23 (a) either 2,3-bornanedione or 2-isopropyl  
24 thioxanthone in an amount of about 0.005 to 0.15% by  
25 weight of the gel and,

26 (b) either ethyl-4-dimethyl amino benzoate or  
27 ethyl-2-dimethyl amino benzoate in an amount of about 2.0  
28 to 7.5% by weight of the gel.  
29

30 69. The method of claim 64 wherein the filler for  
31 the powder component is selected from the group consisting  
32 of barium glass, lithium aluminum silicate, flint silica  
33 and mixtures of the members of this group with each other.  
34  
35  
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1           70. The method of claim 64 wherein the filler for  
2 the powder component contains, by weight of the powder,  
3 16-30% barium glass, 62-70% lithium aluminum silicate and  
4 1-10% flint silica.  
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